GUIDANCE FOR IN-SITU SUBAQUEOUS CAPPING OF CONTAMINATED SEDIMENTS:

Appendix B:
Model for Chemical Containment by a Cap

by

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Introduction

This Appendix describes a model for evaluation of chemical flux through a cap. Through use of this model the effectiveness of chemical containment of a cap can be assessed. This model should be applied once cap design objectives with respect to flux are determined, a specific capping material has been selected and characterized, and a minimum cap thickness has been determined based on components for isolation, bioturbation, erosion, consolidation, and operational considerations. If an objective of the cap is attainment of a given contaminant flux, the model can be used to estimate the required cap thickness.

The effective thickness, L_{eff}, of a cap can be defined as the thickness available for long term chemical containment. This thickness is reduced by consolidation of the cap, $\ddot{A}L_{cap}$, the thickness affected by short term pore water migration due to consolidation in the underlying sediment, $\ddot{A}L_{sed}$, and by bioturbation over a thickness, L_{bio}. Bioturbation, the normal life-cycle activities of benthic organisms, leads to mixing and redistribution of contaminants and sediments in the upper layer. The chemical migration rate within the bioturbated zone is typically much faster than in other portions of a cap. In addition, consolidation typically occurs on a time scale that is rapid compared to the design lifetime of a cap. Consolidation of the cap directly reduces the thickness of a cap and the separation between contaminants and the overlying water and benthic organisms while consolidation of the underlying sediment results in the expression of potentially contaminated porewater. Note, however, that in addition to reducing the thickness of a cap, consolidation serves to reduce both the porosity and permeability of a cap causing reductions in chemical migration rates by both advection and diffusion.

Using $\ddot{A}L_{sed,A}$ to represent the thickness of a cap affected by a contaminant A during consolidation of the underlying sediment, the effective cap thickness remaining for chemical containment is given by

$$L_{eff} = L_0 - L_{bio} - \ddot{A}L_{cap} - \ddot{A}L_{sed,A} \qquad \textbf{(1)}$$

where L_0 is the initial thickness of the cap immediately after placement.

The depth of bioturbation can be assessed through an evaluation of the capping material and recognition of the type, size and density of organisms expected to populate this material. Because of the uncertainty in this evaluation, the bioturbed zone is generally chosen conservatively, that is considered to be as large as the deepest penetrating organism likely to be present in significant numbers. Due to the action of bioturbating organisms, this layer is also generally assumed to pose no resistance to mass transfer between the contaminated sediment layer and the overlying water.

The consolidation of the underlying contaminated sediment can be estimated through consolidation models. The resulting movement of the chemical contaminants must be estimated, however, and a model is described below. The effective cap thickness estimated by Equation (1) is still subject to chemical migration by advection and diffusion

processes. The long term chemical flux to the water via these processes can also be modeled.

The complete model of chemical movement must be composed of two components:

  •An advective component considering the short term consolidation of the contaminated sediment underlying the cap, and,
  •A diffusive or advective-dispersive component considering contaminant movement as a result of porewater movement after the cap has stabilized.

The first component is operative for all caps in which the underlying contaminated sediment layer is compressible but only for a short period of time. The first component allows completion of the determination of the effective cap thickness through Equation (1). The resulting effective cap thickness can then be used to assess long term losses through the cap by advective and/or diffusive processes. For simplicity and conservatism, the sediment underlying a cap could be assumed to remain uniformly contaminated at the concentration levels prior to cap placement. In reality, migration of contaminants into the cap reduce the sediment concentration and the long term flux to the overlying water. The consideration of this situation, however, greatly complicates the analysis and the models used to describe contaminant flux. Both of the model components will be considered separately. Due to the different mechanisms operative in a system with porewater motion present or absent, the second model component will be subdivided into submodels appropriate for each.

Model for Short Term Cap Losses - Advection during Cap Consolidation

After placement of capping materials, consolidation of both the cap and the underlying sediment occurs. Consolidation of the cap results in no contaminant release since the cap is initially free of contamination. Furthermore, the consolidation of the cap serves to reduce the permeability and, to a lesser extent, the porosity of a cap. Both serve to reduce contaminant migration through the cap by both diffusive and advective processes.

Consolidation of the underlying sediment due to the weight of the capping material, however, tends to result in expression of porewater and the contaminants associated with that water. The ultimate amount of consolidation may be estimated using standard methods or computer models. The consolidation of the underlying sediment is likely to occur over a very short period (e.g. months) compared to the lifetime of the cap. It is appropriate, therefore, to assume that the consolidation occurs essentially instantaneously and estimate the resulting contaminant migration solely on the basis of the total depth of consolidation and the porewater expressed. For a nonsorbing contaminant, the penetration depth of the chemical is identical to that of the expressed porewater. For a sorbing contaminant, the penetration depth is less as a result of the accumulation of chemical on the sediment. Mathematically, if $\ddot{A}L_{sed}$ represents the ultimate depth of consolidation of the underlying contaminated sediment due to cap placement, the depth of cap affected by this porewater (or nonsorbing contaminant), $\ddot{A}L_{sed,pw}$, is given by

$$\ddot{A}L_{sed,pw} \approx \frac{\ddot{A}L_{sed}}{\mathring{a}} \qquad (2)$$

where $\mathring{a}$ is the porosity of the cap materials. The division by the cap porosity recognizes that the expressed porewater moves only through the void volume formed by the spaces between the grains of the capping material. Equation (2) assumes that the capping material is spatially uniform and that porewater is not preferentially forced through an area a fraction of the total cap area.

Although the depth of cap affected by the expressed porewater is given by Equation (2), the migration distance of a sorbing contaminant is less due to accumulation in the cap. The quantity of contaminant that can be rapidly adsorbed by the cap material, $\grave{u}_c$ (mg/kg), is generally assumed to be proportional to the concentration in the porewater (C_{pw}, mg/L),

$$\grave{u}_c = K_d^{obs} C_{pw} \qquad (3)$$

where the constant of proportionality is the observed sediment-water partition coefficient. Note that the observed partition coefficient is measured during sorption onto clean cap material. The value of K_d^{obs} may be predicted or measured as described in a subsequent section. Use of a measured value, however, does not require linearity or reversibility of the sorption isotherm, nor does it require specification of the form of the contaminant in the porewater (e.g. dissolved or bound to particles). For a compound that sorbs to soil with an observed partition coefficient of K_d^{obs} (L/kg), the ratio of the total concentration in the soil to that in the porewater is given by the retardation factor, R_f,

$$R_f = \mathring{a} + \tilde{n}_b K_d^{obs} \qquad (4)$$

The distance that the contaminant migrates during underlying sediment consolidation of a distance $\ddot{A}L_{sed}$ is then given by

$$\ddot{A}L_{sed,A} \approx \frac{\ddot{A}L_{sed}}{R_f} \approx \frac{\ddot{A}L_{sed}}{\mathring{a} + \tilde{n}_b K_d^{obs}} \qquad (5)$$

This distance must be subtracted from the actual cap thickness to estimate effective cap thickness.

Note that this model suggests that the more sorbing a cap, the less important is consolidation in the underlying sediment. Sorption for hydrophobic organics such as polyaromatic hydrocarbons and polychlorinated biphenyls is strongly correlated with the organic carbon content of the sediments. If a cap contains 0.5% organic carbon or more, the K_d^{obs} is typically of the order of hundreds or thousands for these compounds and the loss of effective cap thickness by consolidation is a small fraction of the consolidation

distance. Metals also tend to be strongly associated with the solid fraction, again reducing the migration of contaminant out of the sediment as a result of consolidation.

Estimation of Long-Term Losses Mechanisms and Driving Force

The effective cap thickness defined by Equation (1) is subject to advection or diffusion or a combination of both throughout the lifetime of the cap. The long term contaminant release or loss requires estimation of the contaminant flux by these processes. Diffusion is always present while advection only occurs if there exists a significant hydraulic gradient in the underlying sediments. The relative magnitude of diffusion to advection in the cap of effective thickness, L_{eff}, can be estimated by the Peclet number.

$$Pe = \frac{UL_{eff}}{D_{eff}} \qquad \textbf{(6)}$$

where U is the advective velocity (Darcy or superficial velocity) in the sediment and D_{eff} is the effective diffusion/dispersion coefficient. If the magnitude or absolute value of the Peclet number is much greater than one, advection dominates over diffusion/dispersion while the opposite is true for absolute values much less than one. Advection directed out of the cap will speed contaminant release while advection directed into the sediment will effectively lengthen the cap.

The average groundwater flow velocity is estimated from the sediment conductivity (K, cm/sec) or permeability (k, cm^2) and the local hydraulic gradient.

$$U = K \frac{\partial h}{\partial z} = \frac{k\tilde{n}g}{\mu} \frac{\partial h}{\partial z} \qquad \textbf{(7)}$$

Here, ñ is the density of water (~1 gm/cm^3), g is the acceleration of gravity (980 cm·sec^{-2}) and μ is the viscosity of water (~0.01 gm·cm^{-1}·sec^{-1}). $\frac{\partial h}{\partial z}$ is the local gradient in hydraulic head or elevation with distance into the sediment. The average groundwater flow is also the volumetric seepage rate divided by the sediment-water interfacial area. Thus lakes, with large sediment-water interfacial areas tend to exhibit less potential for advective influences than small streams. Estuarine systems subject to significant tidal fluctuations may also exhibit significant advective transport. Losing streams, in which the advective transport is into the sediment may exhibit advection but may not be important since the direction of transport is away from the sediment-water interface and long travel distances may be required to impact groundwater of significance. Similarly, advection may be less important in wetlands subject to frequent cycles of flooding followed by infiltration due to the downward vector of advection. The presence of a cap will tend to reduce any advective transport by preferentially channeling flow to uncapped sediment. The permeability of the cap materials may also be selected to minimize advection.

The effect of advection includes both transport by the porewater flow and that by diffusion and dispersion. Dispersion is the additional "diffusion-like" mixing relative to the average porewater velocity that occurs as a result of heterogeneities in the sediments. Thus the description of advection is more complicated than diffusion and the model for long term cap losses will be subdivided into models appropriate when advection is important and a model appropriate only when diffusion dominates.

Both processes, however, are operative only for that portion of the contaminant present in the porewater. This might include contaminant dissolved in the porewater as well as contaminant sorbed to fine particulate or colloidal matter suspended in the porewater. The pore-water concentration in the underlying sediment, assuming linear partitioning between the sediment and porewater, is given by

$$C_{pw} = \begin{cases} \dfrac{\varpi_{sed}}{K_d} & if \ \dfrac{\varpi_{sed}}{K_d} \leq C^* \\[4mm] C^* & if \ \dfrac{\varpi_{sed}}{K_d} \geq C^* \end{cases} \tag{8}$$

where C^* is the equilibrium solubility of the chemical in water and $\varnothing_{sed}$ is the sediment loading (mg chemical/ kg (dry) sediment). The Equation indicates that the porewater concentration increases linearly with the sediment loading until the water is saturated, that is, until the solubility limit is reached. Loading above that critical value cannot increase the sediment porewater concentration or the driving force for diffusion. The porewater concentration can exceed this value, however, if colloidal organic matter, typically measured by dissolved organic carbon, is present in large quantities in the porewater. Sorption onto this colloidal matter can increase the total fraction of contaminant present in the porewater. If the partitioning to the organic colloidal matter is assumed to be given by $K_{oc,}$ the organic carbon to water partition coefficient, and if $\ae_{oc}$ represents the colloidal organic carbon concentration, then the porewater concentration calculated above must be corrected by the factor $(1+ K_{oc}\ae_{oc})$. This approximately accounts for the enhanced chemical solubility due to the presence of sorbing colloids. A similar correction for metal species could be adopted, however, it is difficult to predict the partitioning of metals to soils and colloidal particles.

Degradation of contaminants over the long time of expected confinement is a significant benefit of capping which should be incorporated into the design of a cap. If simple first order degradation kinetics is employed the sediment loading changes with time according to

$$\varpi_{sed} = \varpi_{sed}^0 \, e^{-k_r t} \tag{9}$$

where ϖ_{sed}^0 is the sediment loading at the time of cap placement and k_r, the exponential time constant is given by $0.693/t_{0.5}$, with $t_{0.5}$ the chemical half life in the sediment.

In the subsequent sections, the sediment porewater concentration estimated by Equation (5) is used to evaluate diffusive and advective-dispersive transport.

Diffusion

Diffusion is a process that occurs at significant rates only within the pores of the sediment and is driven by the difference in porewater concentration between the sediment and the cap. The initial concentration of the contaminant in the cap porewater is generally 0 while the concentration in the sediment is given by Equation(8), modified if appropriate by Equation (9). Even without degradation, however, migration of contaminants into the cap will deplete the underlying sediments as a result of the loss of mass by diffusion through the cap.

Thoma et al. (1993) developed a model of diffusion through a cap that explicitly accounts for depletion in the underlying sediment. A simpler model of diffusion through the cap, however, assumes that the contaminant concentration in the underlying sediment is essentially constant. This would be most appropriate if the contaminant concentration in the sediment far exceeds the critical concentration defined by Equation (8). Because the assumption of no depletion in the underlying sediment overpredicts the driving force for diffusion, however, it also represents a conservative assumption of the effectiveness of the cap. We will therefore employ it in the description that follows.

Let us first estimate the steady long term flux of contaminants through the cap via diffusion. This is the maximum flux that can occur through the cap by the diffusive mechanism.

Maximum Flux Estimation (Steady State) If diffusion is the only operative transport process through the cap, the pseudo steady-state flux through the cap (assuming constant contaminated sediment porewater concentration and no sorption effects in the cap layer) is given by

$$F = \frac{D_w \varepsilon^{4/3}}{L_{eff}} C_{pw} \approx K_{cap} C_{pw} \qquad \textbf{(10)}$$

where

F	=	chemical flux (ng·cm^{-2}·sec^{-1})
D_W	=	the binary diffusivity of the chemical in water, (cm^2/sec)
ε	=	the sediment porosity (void volume/ total volume),
L_{eff}	=	effective cap thickness
C_{pw}	=	pore-water concentration (ng/cm^3)
K_{cap}	=	effective mass transfer coefficient through cap (cm/sec)

Millington and Quirk (1961) suggest the factor $\varepsilon^{4/3}$ to correct for the reduced area and tortuous path of diffusion in porous media. The overlying water concentration is assumed very much less than the sediment porewater concentration.

In general, the chemical flux is influenced by bioturbation and a variety of water column processes. Figure 1 shows the idealized concentration profile in a capped system at this pseudo steady state. The flux of chemical through each layer is equal to the sum of the rate of evaporation and flushing.

Mathematically, in terms of mass transfer coefficients, we have:

$$M = K_{ov} A_s \ C_{pw} = K_{cap} A_s (C_{pw} - C_{bio}) =$$
$$K_{bio} A_s (C_{bio} - C_{sw}) = K_{bl} As (C_{sw} - C_w) = (K_e A_e + Q) C_w$$

(11)

where

M	=	rate of chemical loss from the system (mg/day) = $F*A_s$
K_{ov}	=	overall mass transfer coefficient (cm/day)
A_S	=	contaminated sediment area (m^2)
A_e	=	evaporative surface area (m^2)
K_{cap}	=	cap mass transfer coefficient = D_w å$^{4/3}$ /L$_{eff}$ (cm/day)
C_{pw}	=	porewater concentration within the contaminated sediment Including dissolved and any sorbed to colloidal material
C_{bio}	=	porewater concentration at the top of the cap (ng/cm^3)
C_{sw}	=	porewater concentration at the sediment water interface (ng/cm^3)
K_{bio}	=	bioturbation mass transfer coefficient = $\dfrac{ç D_{bio} \ R_f}{L_{bio}}$ (cm/day)
ç	=	desorption efficiency of contaminant from sediment particles (0.1-0.2)
D_{bio}	=	biodiffusion coefficient (cm^2/day)
R_f	=	retardation factor = å + ñ$_B$$K_d^{obs}$
L_{bio}	=	depth of bioturbation (cm)
K_{bl}	=	benthic boundary layer mass transfer coefficient (cm/day)
K_e	=	evaporation mass transfer coefficient (cm/day)
D_e	=	effective diffusivity = $D_w \cdot$ å$^{4/3}$ (cm^3/day)
Q	=	basin flushing rate (cm^3/day).
C_w	=	chemical concentration in the basin water (ng/cm^3).
K_d	=	sediment water partition coefficient for the chemical = $K_{oc} f_{OC}$ (cm^3/g)
K_{oc}	=	organic carbon-water coefficient for the chemical (cm^3/g)
f_{oc}	=	sediment fractional organic carbon content.
ñ$_B$	=	sediment bulk density.

The overall mass transfer coefficient, K_{ov}, can be obtained from the following:

$$\frac{1}{K_{ov}} = \frac{1}{K_{cap}} + \frac{1}{K_{bio}} + \frac{1}{K_{bl}} + \frac{A_s}{K_e A_e + Q}$$

(12)

An analysis of this relationship for reasonable values of L$_{eff}$ suggests that *1/K_{ov}* $\cong$ *1/K_{cap}* and therefore the cap controls the flux to the overlying water and Equation ((10)) is valid.

This flux can be used to estimate water concentrations in the water (*C_W*) or at the sediment water interface (*C_{SW}*) or multiplied by the capped area to determine total release rate. For hydrophobic organics, the concentration in the overlying water at steady-state is defined by a balance between the flux through the cap, the rate of evaporation to the air and the

rate of flushing of the water column. For metals and elemental species not associated with volatile compounds, the flux through the cap is balanced only with the flushing of the water column. The overlying water concentration of the contaminant is given by:

$$C_w = \left(\frac{K_{ov} \, A_s}{K_e \, A_\ell \, + \, Q} \right) C_{sed} \tag{13}$$

The concentration at the sediment-water interface, which would be indicative of the level of exposure of bottom surface dwelling organisms, is defined by the balance of the flux through the cap with the flux through the benthic boundary layer. The contaminant concentration at the sediment-water interface is:

$$C_{Sw} = \frac{K_{ov} \, C_{sed}}{K_{b\ell}} \, + \, C_w \tag{14}$$

Either of these concentrations or the estimated fluxes may be compared to applicable criteria for the chemical in question to determine if a specified cap thickness is adequate. A sample calculation is presented below.

Transient Diffusion - Breakthrough time estimation. The simple steady state analysis we have presented above is not capable of predicting the time required for the contaminant(s) to migrate through the cap layer. Until sorption and migration in the cap is complete, the flux to the water column will be less than predicted by Equation (10). Time must be explicitly incorporated in the differential mass balance to address this problem. The following partial differential equation represents a differential mass balance on the contaminant in the pore-water of the cap as it diffuses from the contaminated sediment below.

$$R_f \, \frac{\partial C_{pw}}{\partial t} = D_w \mathbf{g}^{4/3} \, \frac{\partial^2 C_{pw}}{\partial z^2} \tag{15}$$

We apply the conditions of a constant concentration at the sediment-cap interface as specified by Equation (8) and effectively zero concentration at the height L_{eff} in the cap. Carslaw and Jaeger (1959) present a solution to the equivalent heat transfer problem which in terms of concentration and mass diffusion is given by:

$$F_{diff} = \frac{C_{pw} D_{eff}}{L_{eff}} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{D_{eff} \{n\eth\}^2 t}{R_f L_{eff}^2} \right) \right] \tag{16}$$

where D_{eff} represents $D_w å^{4/3}$. Note that as $t \to \infty$ the expontential term in square brackets approaches zero and the flux approaches the value obtained by the approximation $K_{ov} \approx D_{eff} / L_{eff}$ as indicated by Equation (10). From Equation (16) we can obtain relations for the breakthrough time and the time required to approach the steady state flux.

We define breakthrough time, $\hat{o}_b$, as the time at which the flux of contaminant from the contaminated sediment layer has reached 5% of its steady state value, and we define the time to reach steady state, $\hat{o}_{ss}$, as the time when the flux is 95% of its steady state value. It is easily shown that

$$\hat{o}_b = \frac{0.54 L_{eff}^2 R_f}{D_w \mathbf{g}^{4/3} \check{o}^2} \tag{17}$$

and

$$\hat{o}_{ss} = \frac{3.69 L_{eff}^2 R_f}{D_w \mathbf{g}^{4/3} \check{o}^2} \tag{18}$$

Advective-Dispersive Models

When advection cannot be neglected during the operation of a cap, the basic equation governing contaminant movement is

$$R_f \frac{\partial C_{pw}}{\partial t} + U \frac{\partial C_{pw}}{\partial z} = D_{eff} \frac{\partial^2 C_{pw}}{\partial z^2} \tag{19}$$

where C_{pw} is the contaminant concentration in the porewater. U is again the Darcy velocity and D_{eff} is the effective diffusion/dispersion coefficient. The effective diffusion/dispersion coefficient is often modeled by a relationship of the form

$$D_{eff} = D_w \mathring{a}^n + \acute{a} U \tag{20}$$

The first term in this relation is associated with molecular diffusion and is identical to the effective diffusivity used above.

The second term is mechanical dispersion associated with the additional mixing due to flow variations and channeling. á is the dispersivity and is typically taken to be related to the sediment grain size (uniform sandy sediments) or travel distance (heterogeneous sediments). Very little guidance exists for the estimation of field dispersivities for vertical flow in sediments. In uniform sandy sediments, the dispersivity is approximately one-half the grain diameter. Dispersion in heterogeneous sediments would be expected to be larger.

If the effective dispersivity can be estimated, the contaminant concentration and flux through the cap can be estimated by solutions to Equation (19). Let us first consider the long time behavior of Equation (19) when the sediment originally exhibits a contaminant

porewater concentration C_0. If the contaminant is not subject to depletion by either degradation or migration through the cap, the flux through the cap, at infinitely long time periods, ultimately reaches that given by

$$F_{adv} \rightarrow U\, C_0 \qquad as\ t \rightarrow \infty \qquad\qquad \textbf{(21)}$$

That is, once the adsorbing capacity of the cap is exhausted, the contaminant flux due to advection is identical to that which would be observed if no cap were placed over the sediment.   Recognize that any sorption in the cap must deplete the reservoir of contaminants in the contaminated layer. The assumption of no depletion is therfore very conservative.

In the advection dominated case, therefore, it is important to examine the transient release of the contaminant.   The conditions on Equation (10) that are appropriate for a cap

$$
\begin{aligned}
cap\text{-}sediment\ interface\ (z=0) &\quad C_{pw} = C_0 \\
cap\text{-}water\ interface\ (z=L_{eff}) &\quad C_{pw} = C_w \qquad (Generally\ C_w \\
initial\ cap\ concentration &\quad C_{pw} = 0
\end{aligned}
\qquad \textbf{(22)}
$$

include Available solutions, however, do not satisfy the cap-water interface condition. Instead there are two solutions that are commonly applied.

$$
\begin{aligned}
\frac{\partial C_{pw}}{\partial z} &= 0 \qquad at\ z = L \qquad (finite\ cap) \\
\frac{\partial C_{pw}}{\partial z} &= 0 \qquad as\ z \rightarrow \infty \quad (infinite\ cap)
\end{aligned}
\qquad \textbf{(23)}
$$

The first explicity recognizes the finite thickness of the cap while the second assumes that it is infinitely thick. For Pe>1, however, the solution to Equation (10) subject to either condition is essentially identical. Moreover, for Pe<1 when diffusion dominates, the finite cap condition is inappropriate and causes the solution to underpredict the contaminant flux through the cap. The solution for the infinite cap is also simpler to use. For these reasons, only the infinite cap thickness model will be described here.

The solution to Equation(19) subject to the infinite cap condition is given by

$$,t) \;=\; \frac{C_0}{2}\left[erfc\left(\frac{R_f\; z\; -\; Ut}{2\sqrt{R_f\; Dt}} \right) \;+\; \exp\left(\frac{Uz}{D} \right) erfc\left(\frac{R_f\; z\; -}{2\sqrt{R_f}} \right. \right. \tag{24}$$

Here erfc represents the complementary error function which is given by 1- erf, the error function. The error function is a tabulated function (e.g.,Thibodeaux, 1979) and is commonly available in spreadsheets and computer languages. It ranges from 0 at a value of the argument equal to zero to 1 at a value of the argument equal to infinity. The model is most useful in predicting the penetration of the contaminant into the cap and the time until the sediment-water interface begins to be significantly influenced by the cap, the breakthrough time. The breakthrough time can be estimated by evaluating Equation (24) for z=L_{eff} and determining the time required until $C_{pw}(L_{eff},t)$ is equal to some fixed fraction of the concentration in the underlying sediment, for example until $C_{pw}(L_{eff},t)=0.05\ C_0$. The flux at any time could also be evaluated by computing

$$F_{adv/disp} \;=\; U\; C_{pw}(L_{eff},t) \;-\; D_{eff}\; \frac{\partial C_{pw}}{\partial t} \tag{25}$$

The equation for the flux is lengthy, however, and, as indicated earlier, Equation(24) is most useful to calculate the breakthrough time or the concentration profile within the cap at any given time.

Parameter Estimation

Use of any of the equations presented above requires estimation of a variety of model parameters. The most important of these parameters and an example calcuation are presented below.

These include the porosity($\mathring{a}$), bulk density($\tilde{n}_b$) and organic carbon content (f_{oc}) of the cap material, the partition coefficient(K_d) for the chemical(s) between the pore-water and the cap material, the diffusivity of the chemical(s) in water(D_W), the depth of bioturbation(b) and a biodiffusion coefficient(D_{bio}), benthic boundary layer(k_{bbl}) and evaporation(K_e) mass transfer coefficients, and for flowing systems the water depth(H) and current velocity(v). Information should be obtained on the degradadion half-life or reaction rate of chemicals of concern in the specific project if such information is available.

Contaminant properties These include water diffusivity and sediment-water or cap-water partition coefficient. The water diffusivity of most compounds varies less than a factor of two from 1×10^{-5} cm^2/sec. Higher molecular weight compounds such as PAH's tend to have a water diffusivity of the order of 5×10^{-6} cm^2/sec. Estimation techniques can be found in Lyman et al. (1990). The preferred means of determining the partition coefficient is through experimental measurement of sediment and porewater concentration in the sediment or cap. In this manner, any sorption of contaminant onto suspended particulate or colloidal matter is implicitly incorporated. If such measurements are unavailable, it is possible to predict values of the partition coefficient, at least for hydrophobic organic compounds. For other contaminants, including metals, very little predictive guidance

$$K_d^{obs} = \frac{K_d}{1 + \tilde{n}_{oc} K_{oc}} \qquad\qquad (26)$$

exists. For hydrophobic organics, the partition coefficient between the pore-water and sediment for a given chemical can be estimated from the organic carbon-water partition coefficient through the relation $K_d = f_{oc} K_{oc}$. K_{oc} values are tabulated (e.g. Montgomery and Welkom, 1990) or may be estimated from solubility or the octanol-water partition coefficient using the methods in Lyman et al. (1990). If colloidal material in the porewater influences the partition coefficient, an apparent or effective partition coefficient can be estimated from the dissolved organic carbon concentration, $\tilde{n}_{oc}$, in the porewater and the relationThe porewater concentration to be used in this case is then not the truly dissolved concentration but that corrected for the amount sorbed on the colloidal matter. This is the same correction for the presence of colloidal matter referred to in the discussion of Equation (8).

Physical characteristics The long term average current velocity and water depth should be evaluated for the site to determine water side mass transfer resistances. Cap material properties are dependent on the specific materials available and should be measured using standard analytical methods. The water diffusivity can be estimated using the Wilke-Chang method (Bird *et al.,* 1960). Compilations of diffusivities are also available (Thibodeaux, 1979; Montgomery and Welkom, 1990).

Mass transfer coefficients A turbulent mass transfer correlation (Thibodeaux, 1979) can be used to estimate the value of $K_{b\ell}$ in the water above the cap:

$$Sh = 0.036\ Re^{0.8}\ Sc^{1/3} \qquad\qquad (27)$$

where Sh =   Sherwood number = $\dfrac{K_{b\ell} \cdot x}{D_w}$

              Re =   Reynolds number = $\dfrac{x \cdot u}{\acute{\imath}}$

              Sc =   Schmidt number = $\dfrac{\acute{\imath}}{D_w}$

              $\acute{\imath}$ =   kinematic viscosity of water, (0.01 cm²/sec at 20°C)

              u =   benthic boundary layer water velocity (cm/s)

              x =   length scale for the contaminated region - here we take $x = \sqrt{A_s}$ (cm), where A_s is the surface area of the contaminated region

As indicated previously, however, the benthic boundary layer mass transfer coefficient is rarely significant in the estimation of contaminant flux through the cap.

Transport by bioturbation has often been quantified by an effective diffusion coefficient based on particle reworking rates. A bioturbation mass transfer coefficient can then be estimated from the following relation assuming linear partitioning between the sediment and water in the bioturbation layer

$$K_{bio} = \frac{D_{bio} \tilde{n}_b K_d \varsigma}{L_{bio}} \qquad \textbf{(28)}$$

where ç is a desorption efficiency of the chemical once the particle carrying it has been reworked to the sediment-water interface. ç would tend to be small for more hydrophobic compounds thattend to desorb slowly at the surface and large for compounds that are more soluble. In the absence of experimental information to the contrary, ç is assumed to be 1. The biodiffusion coefficient and the depth of bioturbation are important factors in the determination of the required cap thickness, and thus the best possible estimates should be used. The ranges for D_{bio} and L_{bio} are quite large, and an extensive tabulation is presented by Matisoff (1982). An examination of this data suggests that a depth of bioturbation of 2-10 cm is typical and that biodiffusion coefficients are generally in the range of 0.3-30 cm^2/yr. As indicated previously, however, the contaminant flux is controlled by transport through the cap and is essentially insensitive to the bioturbation mass transfer coefficient.

Evaporation mass transfer coefficient Evaporation from natural, unagitated surfaces is normally water side controlled for sparingly soluble compounds such as those of interest in this discussion. We will take the overall evaporation mass transfer coefficient as equal to the water-side mass transfer coefficient. A water-side mass transfer coefficient for evaporative losses is given by Lunny (1983) as

$$K_e = 19.6 U_x^{2.23} D_w^{2/3}$$

where U_x is the wind speed at 10m (miles/hr), D_w has units of cm^2/sec, and K_e has units of cm/hr.

Cap technical design. Several design criteria are possible for specifying the physico-chemical containment afforded by a cap. There are at least five quantities which may be of interest to the cap designer and for which models were presented here. These are the breakthrough time, the pollutant release rate (as an source term input to other fate and effects models), concentrations at the sediment-water interface or in the overlying water column and the time to approach steady state. The two physico-chemical properties of the cap material which have the largest effect on the efficacy of the cap are the organic carbon content and the cap thickness. We will illustrate the design procedure for choosing the proper cap thickness and estimating the breakthrough time in the following example.

Example calculation of cap thickness. Table 1 presents parameter values used for estimating polychlorinated biphenyl release from New Bedford Harbor sediments (Thibodeaux and Bosworth, 1990).

Table 1. Physico-Chemical Properties of Site Parameters		
Cap Properties		
Organic carbon content	(f_{oc})	0.005
Porosity	(ϵ)	0.25
Bulk density	$(\tilde{n}_b)$	2.0 g/cm^3
Colloid concentration	(C_c)	20 mg/L
Effective cap thickness	(L_{eff})	35 cm
Aroclor 1242 Properties		
Solubility (salt water)	(s)	88 µg/L
Diffusivity in Water	(D_w)	4.5 x 10^{-6} cm^2/sec
Organic Carbon Partition Coeff.	(K_{oc})	198000 L/kg
Evaporative Mass Transfer Coeff.	(K_e)	7 cm/hr (Thibodeaux and Bosworth, 1990)
Site Properties		
Bioturbation Depth	(L_{bio})	10 cm
Biodiffusion Coefficient	(D_{bio})	10 cm^2/yr
A1242 sediment loading	$(\grave{u}_A)$	500 mg/kg
Extent of contamination	$A_s)$	10000 m^2
Evaporative mass transfer area	A_e	10000 m^2
Benthic Boundary Layer Velocity	(u)	10 cm/sec
Basin flushing rate	(Q)	1.7 x 10^{13} cm^3/day
Water Quality Criterion	(C_{WQC})	30 ng/L

Air

$$N_A = (K_e A_e + Q) C_w$$

Water

$$N_A = K_{bl}(C_{sw} - C_w)$$

Benthic BL

Bioturbation zone

$$N_A = K_{bio}(C_{bio} - C_{sw})$$

$$N_A = K_{cap}(C_{sed} - C_{bio})$$

Cap

Concentration profile
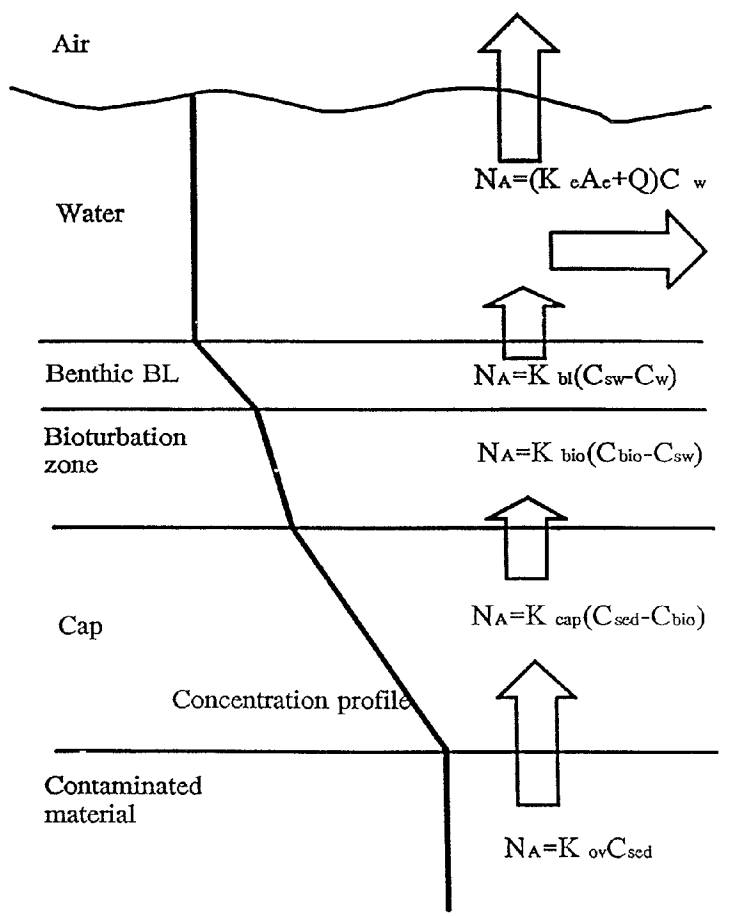
Contaminated material

$$N_A = K_{ov} C_{sed}$$

Figure B-1. Idealized contaminant concentration in a cap and sediment profile and flux relationships.

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